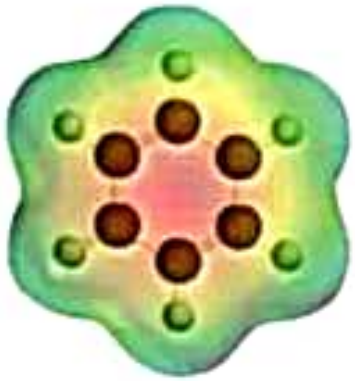
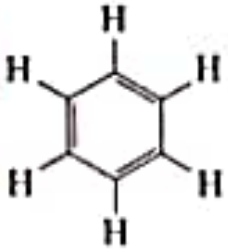
DELOCALIZATION IN CHEMICAL BONDING TERMINOLOGIES

Delocalized electrons:

The electrons which neither belong to a single atom nor are confined to a bond between two atoms, but are shared by three or more atoms.

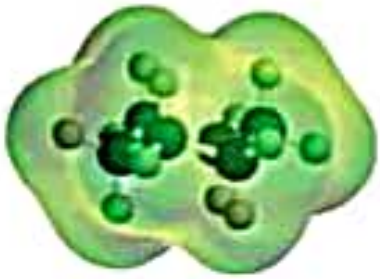


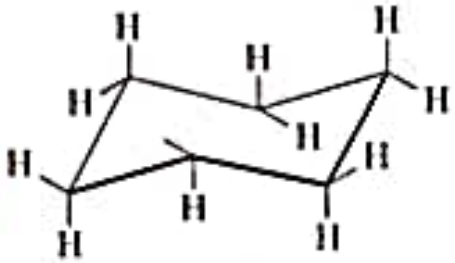


benzene

Localized electrons:

Electrons that are restricted to a particular region. i.e electrons which remain fixed in its position as that of single bond.





cyclohexane

Conjugated system

A system or molecule which have alternate single and double bonds.

$$CH_2=CH-CH_2-CH=CH_2$$

DELOCALIZATION

The process of bond formation involving delocalized electrons. Delocalization is characteristic of pi electrons, where the pi electrons changes it position in between different sub orbitals (changes location)

Conjugation (Origin of the Electron Delocalization Phenomenon)

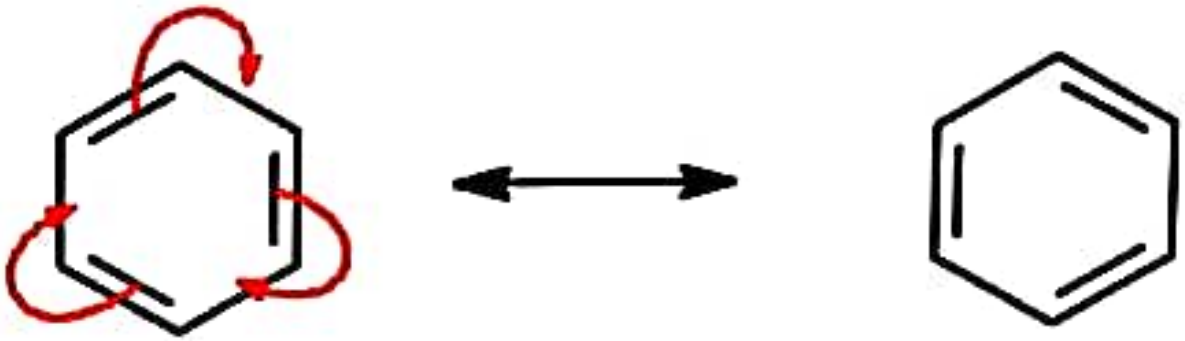
- a conjugated system is one in which overlap of p orbitals occurs "across" what would be considered pure sigma-bonds If we only consider Lewis structures, simple Lewis structures are "deficient" in situations like this, conjugated systems result in electron DELOCALIZATION, as in the example given above

- The definition of a conjugated system is one that consists of ADJACENT atoms that have p atomic orbitals that can overlap "sideways" to form an extended pi-system.

- due to delocalization of electrons delocalized bond is formed by fluctuation of pi bonds resulting in different structures known as resonance / contributing structures.

HOW ?

If we focus on the orbital pictures, we can immediately see the potential for electron delocalization. The two pi molecular bonds shown in red on the left below are close enough to overlap. Overlapping is a good thing because it delocalizes the electrons and spreads them over a larger area, bringing added stability to the system and fluctuate hence resonance occur.



WHY DELOCALIZATION OCCUR ?

- ✓ Delocalization is characteristic of pi bond .
- ✓ It occur due to presence od double and triple bond which is characteristic of hybridization.
- ✓ Delocalization involves sp2 sp3 and other complex hybridizations.
- ✓ The main factor which influences delocalization is excess availability of sub orbitals of about same energy then that of the number of electrons.
- ✓ Delocalization is carried out by forming delocalized bond to maintain the the stability of the molecule.
- ✓ Delocalized bonding (resonance) exists for molecules that differ only in the allocation of single and double bonds to the same kind of atoms.

TYPES OF DELOCALIZATION

Delocalization in chemical bond is carried out in different ways in different systems some of which are as follows.

1=Delocalization in isolated systems

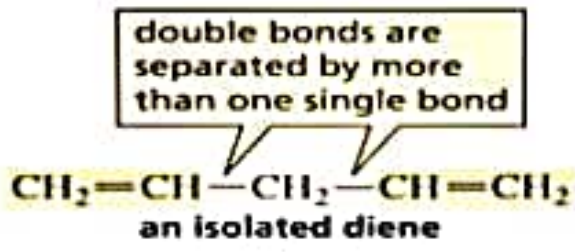
double bonds are separated by more than one single bond

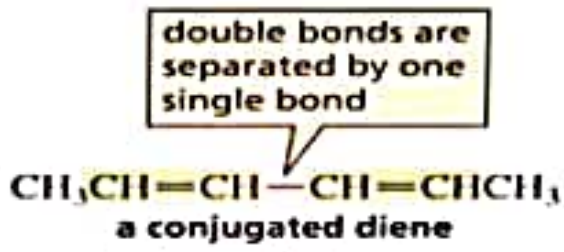
2=Delocalization in conjugated systems

If there is alternate single and double bond exists e.g benzene

3=Delocalization in cumulated systems

If double bonds are adjacent to each other e.g 1,2-dipropene H2C=C=CH2





1=Delocalization in isolated systems

a system having double bonds are separated by more than one single bond.

e.g 

Explanation

- ✓ This structure is 1,4-pentadiene and is isolated system.
- ✓ Each carbon in this system is sp2 hybrid.
- ✓ Each carbon as normal can form 4 single bond but here isolated system is formed by placing two pi bonds
- ✓ The pi orbitals lie perpendicular to the plane
- ✓ Each carbon forms a sigma bond with hydrogen as well as with another carbon atom.
- ✓ Two pi bond are formed (half above the plane and half below) among pi orbitals.
- ✓ The bonds not retain a position but fluctuate its position forming isomers or contributing structures.

3=Delocalization in cumulated systems

If double bonds are adjacent to each other e.g 1,2-dipropene H2C=C=CH2
OR When both sets of double bonds emanate from the same carbon,

- ✓ Each carbon in this system is sp2 hybrid.
- ✓ Each carbon as normal can form 4 single bond but here cumulated system is formed by placing two pi bonds
- ✓ The pi orbitals lie perpendicular to the plane
- ✓ Each carbon forms a sigma bond with hydrogen as well as with another carbon atom.Two pi bond are formed (half above the plane and half below) among pi orbitals.
- ✓ The bonds not retain a position but fluctuate its position forming isomers or contributing structures

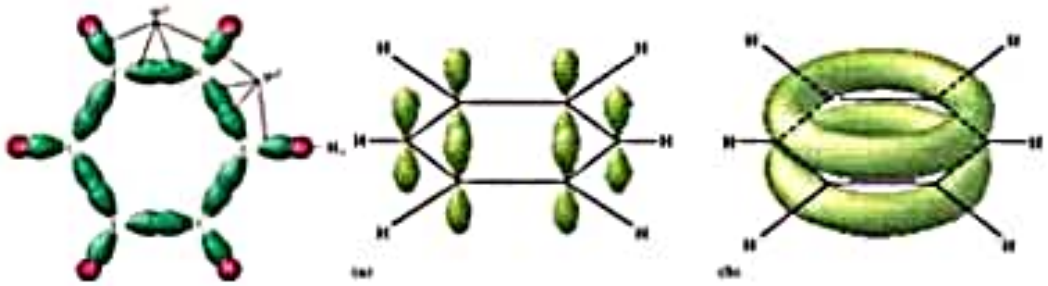
Delocalization in conjugated systems

The definition of a conjugated system is one that consist of ADJACENT atoms that have p atomic orbitals that can overlap "sideways" to form an extended pi-system. Or If there is alternate single and double bond exist in a system ,is known as conjugated system e.g benzene

Example

Delocalization in benzene

- ✓ **Benzene is conjugated aromatic system having a planner structure.**
- ✓ **Consist of six carbons involving alternate bond system**
- ✓ **Each carbon is sp2 hybrid.**
- ✓ **Carbon–carbon and carbon–hydrogen s bonds.**
- ✓ **Carbon p-orbitals overlap with neighbors.**
- ✓ **Cloud of p electrons occur above and below ring.**
- ✓ **Benzene is planar and six p orbitals are parallel. P orbitals are close enough for side-to-side overlap.**
- ✓ **Overlapping p orbitals form a doughnut-shaped cloud of electrons above and below the benzene ring.**
- ✓ **All C-C bonds have the same electron density.**



a)The sigma bond framework **b)Unhybridized p-orbitals** **c) Pi bonding delocalization**

EFFECTS OF DELOCALIZATION

Characteristics

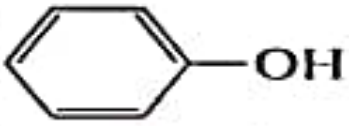
- Delocalization is a character of sp2 hybridization
- Pi electrons influence it.
- Delocalization results in resonance, mesomeric effects and isomerism.
- Hyperconjugation is also result of delocalization.

Chemical Consequences of Electron Delocalization

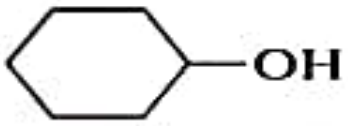
1.Increase acidity

a.Carboxylic acids (RCOOH) are much more acidic than and alcohols (ROH)

b.A protonated aniline is more acidic than a protonated cyclohexylamine



phenol
$pK_a = 10$



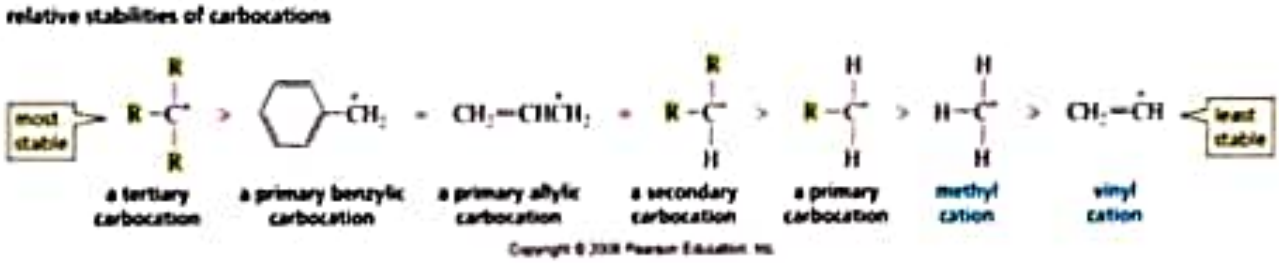
cyclohexanol
$pK_a = 16$

CH_3CH_2OH

ethanol
$pK_a = 16$

B.increse stability

Because allylic cation and benzylic cation have delocalized electrons, they are more stable than other primary carbocations.



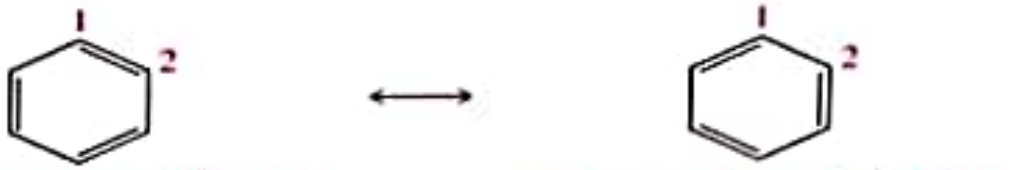
c.Increse dipole moment

due to delocalization elecrons involve in resonance and increase dipole moment.

RESONANCE

When it is possible to draw more than one valid Lewis diagram for a molecule or ion, that species is said to have resonance (electrons are delocalized).

- **The molecule or ion is said to be a resonance hybrid of the structures drawn.**
- **The approximate structure with localized electrons is called a resonance contributor.**
- **The actual structure with delocalized electrons is called a resonance hybrid.**

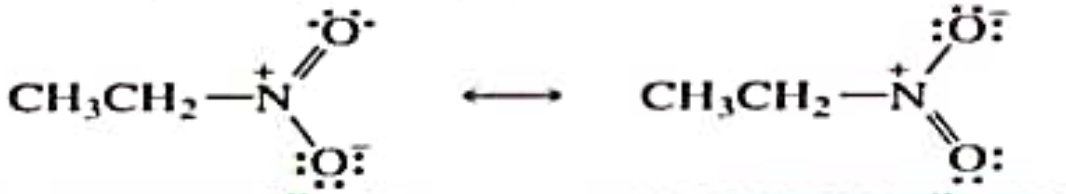


resonance contributor ⟷ resonance contributor

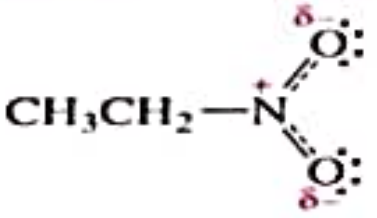
resonance hybrid

How to Draw Resonance Contributors

Delocalized electrons result from a p orbital overlapping the p orbitals of more than one adjacent atom.



resonance contributor ⟷ resonance contributor



resonance hybrid

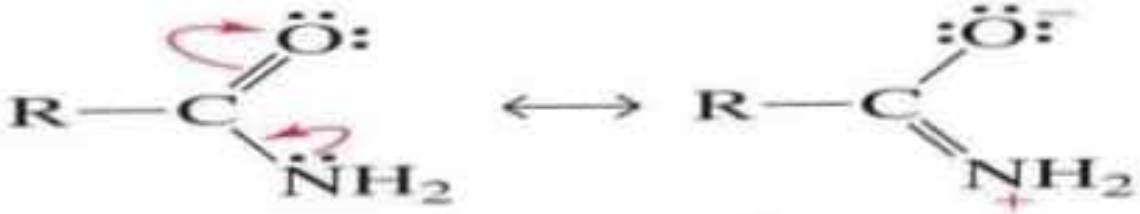
Rules for Drawing Resonance Contributors

- Only electrons move. The nuclei of the atoms never move.
- The only electrons that move are p electrons or lone-pair electrons.
- The total number of electrons in the molecule doesn't change. All resonance contributors have the same net charge.
- Electrons are always moved toward an sp2 carbon.
- An sp2 carbon is either a positively charged carbon or a double-bonded carbon.

resonance contributors

resonance hybrid

- Electrons cannot be moved toward an sp3 carbon, because an sp3 carbon cannot accept any more electrons, it has a complete octet.
- Moving lone-pair electrons toward an sp2 carbon.
- The sp2 carbon can accommodate the new electrons by breaking a π bond.



resonance contributors

resonance hybrid

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THE END